Vitreous State Laboratory

The Catholic University of America

Washington, D.C. 20064

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ADDITIVITES

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OF C$_{10}$ HYDROCARBON MIXTURES

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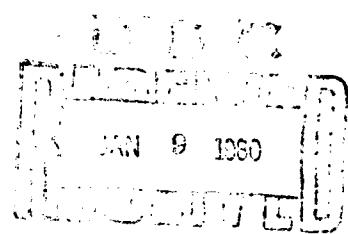
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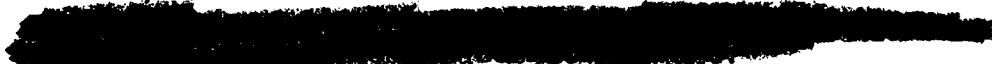
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Shear viscosities and densities have been measured from 50°C to as low as -56°C for n-decane, n-butyl cyclohexane, cis-decalin, 2,7-dimethyloctane, n-butyl benzene, and their mixtures. A simple semi-empirical equation based on the assumption of additivity of free volumes was applied to mixtures of the first three of these and gives quite good predictions of the combined temperature-composition dependence of the viscosity of these systems. A substantial fraction of the viscosity differences among these

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three liquids can be accounted for simply on the basis of
differences in the sizes of the molecules.

INTRODUCTION

The research sponsored under the present contract is concerned with the development of semi-empirical rules to predict the temperature and composition dependence of shear viscosity of hydrocarbon mixtures in the molecular weight range of those encountered in jet fuels. In this report we present experimental results of a study of shear viscosities of mixtures of the five C_{10} hydrocarbon liquids shown below.
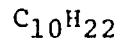
n-decane (ND)   n-butylcyclohexane (NBC)   cis-decalin (CD)

$C_{10}H_{22}$ $C_{10}H_{20}$ $C_{10}H_{18}$
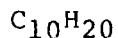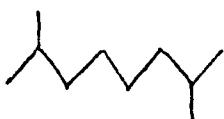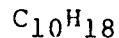
2,7-dimethyloctane (DMO)   n-butylbenzene (NBB)
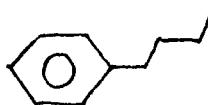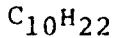
$C_{10}H_{22}$ $C_{10}H_{14}$
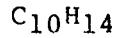
Simple isothermal additivity rules were tested for calculating the viscosities of the mixtures in terms of those of the pure components. In addition, for mixtures of the first

three hydrocarbons listed above (ND,NBC, and CD) preliminary fits were made to an expression based on the free volume theory which accounts for the combined composition/temperature dependence of the shear viscosity.

EXPERIMENTAL SECTION

Samples of n-decane (99+ %), n-butylcyclohexane (99+ %), cis-decalin (99%), and n-butylbenzene (99+ %) were obtained from the Aldrich Chemical Company. 2,7-dimethyloctane (99%) was obtained from Chemical Samples Company. All were used without further purification.

Shear viscosities η and densities ρ were measured for the five neat hydrocarbons, all ten binary 0.5-0.5 mixtures, four ternary 1/3-1/3-1/3 mixtures, one quaternary 0.25-0.25-0.25-0.25 mixture, and one quinternary 0.2-0.2-0.2-0.2-0.2 mixture, where all compositions are in mole fraction. In addition, η and ρ were determined for the 0.25-0.75 and 0.75-0.25 CD/DMO binary mixtures. The temperature ranges of measurement were from 50° down to either about -55°C or the temperature above this where the sample crystallized. The melting points of pure NBC (-75°C), DMO (-55°C), and NBB (-88°C) are at the lower limit of or below the temperature range of this study. The melting point of CD (-43°C) is within this range, but CD was stable under supercooling and did not crystallize. ND (m.p. = -30°C) and most of the mixtures containing substantial amounts of it could be supercooled very little, if at all, and crystallized quite reproducibly whenever the temperature dropped below a certain critical value. These temperatures were about -31°C for p··

ND, -40°C for 0.5 ND - 0.5 NBC, -44°C for 0.5 ND - 0.5 CD, -45°C for 0.5 ND - 0.5 NBC, -51°C for 1/3 ND - 1/3 NBC - 1/3 CD, and -51°C for 1/3 ND - 1/3 CD - 1/3 NBB.

Kinematic viscosities ν were measured with factory calibrated Cannon-Ubbelohde viscometers. Densities ρ were measured at the same time as the viscosities in a dilatometer of about 11 mL volume constructed by sealing a portion of a graduated 5 mL pipette stem to a 10 mL volumetric flask; liquid volumes could be read to the nearest 0.01 ml. The dilatometer was calibrated using deionized water as a density standard. The shear viscosity η was obtained as the $\nu\rho$ product. The viscometers and dilatometer were thermostatted to within about $\pm 0.05°C$ or better in a regulated water bath above room temperature and in a regulated refrigerated methanol bath below room temperature. Bath temperatures were determined with a copper-constantan thermocouple which had been calibrated against a NBS certified Pt resistance thermometer.

The accuracy of the density is estimated to be 0.1%. Taking into account uncertainties in ρ (0.1%), uncertainties in temperature T ($\pm 0.05°C$, which gives about 0.05% uncertainty in η at the highest T's and 0.2% at the lowest T's), uncertainties in viscometer efflux times (0.1 - 0.2%), and the uncertainty in the viscometer calibration constant (0.1%), the overall accuracy of η should be in the range 0.4% to 0.6%.

RESULTS

Within experimental error densities were linear functions of temperature and are given Table I in the form of least squares fits to the equation

$$\rho(g/cm^3) = \rho_0 - bT(^\circ C) \tag{1}$$

Duplicate density results (Runs I and II) were obtained for five of the entries in Table I and agree within our estimated uncertainty of 0.1% or better, as may be seen by comparing the values of ρ_0 (ρ at 0°C) and the density temperature coefficients b.

Typical viscosity results are shown in the form of Arrhenius plots (log η vs. $10^3/T(K)$) in Fig. 1 for the five neat hydrocarbons. Note that the viscosity difference between any two liquids becomes larger the lower the temperature. The temperature dependence of the viscosity of each liquid could be described within experimental error by the semi-empirical VTF equation:

$$\ln \eta(P) = A + B/(T(K) - T_2) \tag{2}$$

where A, B and T_2 are constants. The best fit VTF equation parameters (to the nearest 1 K in T_2)[1] are given in Table II. In this context the VTF equation can be considered as a smoothing function for η vs. T, so that the parameters of Table II can be used to calculate η at any T in the experimental region.

Smoothed experimental viscosities at integral temperatures obtained from Eq. (2) and the parameters of Table II are compared for duplicate viscosity determinations for five liquids in Table III. The agreement between the duplicate runs is well within our estimated experimental accuracy in η.

DISCUSSION

Isothermal Viscosity Additivity Rules

We tested three simple isothermal additivity rules for expressing mixture viscosities in terms of the viscosities of the pure components.

additivity of viscosities

$$\eta = \Sigma X_i \eta_i \tag{3}$$

additivity of fluidities

$$\eta = (\Sigma X_i / \eta_i)^{-1} \tag{4}$$

logarithmic additivity of viscosities or fluidities

$$\eta = \exp(\Sigma X_i \ell n \eta_i) \tag{5}$$

where X_i is the mole fraction and η_i the viscosity of pure component i.

Equation (3) grossly overestimated mixture viscosities, and will not be discussed further. Tests of Eqs. (4) and (5) are illustrated in Table IV, where ratios of calculated to experimental mixture viscosities are tabulated at two

temperatures, and in Fig. 2, where isotherms of $\log \eta$ vs. X_{CD} are plotted for the CD-DMO binary system.

Equation (5) uniformly tends to overestimate mixture viscosities, and the errors become larger the greater the difference between the viscosities of the pure components, i.e., the lower the temperature.

Equation (4), which assumes isothermal additivity of fluidities, gives the best agreement with the experimental viscosities. Two general trends are immediately apparent from the ratios of calculated to experimental viscosity in Table IV.

1. For binary, mixtures of the saturated hydrocarbons (ND, NBC, CD, DMO) Eq. (4) uniformly underestimates viscosities, and the errors become larger the larger the differences in the pure component viscosities, i.e., the lower the temperature.

2. For binary mixtures of the aromatic hydrocarbon NBB with the saturated hydrocarbons Eq. (4) overestimates the mixture viscosities. These two effects, i.e., viscosity underestimates which become larger the greater the difference in component viscosities and viscosity overestimates when a saturated and aromatic hydrocarbon are mixed, compensate one another in mixtures in which both effects are important. For example, in the quinternary mixture Eq. (4) correctly predicts the viscosity within 2% or better. This is apparently due to the compensating effects of the high viscosity component CD and the aromatic NBB.

Master Viscosity Equation

In this section we discuss preliminary results of efforts to discover a master viscosity equation which will account for the combined composition/temperature dependence of the viscosities of the liquids studied here. These preliminary efforts have been confined to results for only three of the hydrocarbons -ND, NBC and CD.

The B parameters for the best fits to the VTF equation in Table II for liquids containing only these three components are all nearly the same; the mean value (using only the Run I values where duplicate experiments were run) is 641.1. Using this mean value of B VTF equation fits to the viscosities of these liquids could be obtained which were only slightly worse than the best fits of Table II. Parameters for VTF equation fits using this constant B value are given in Table V. (These fits are for Run I where duplicate experiments were run.) Inspection of these parameters shows that forcing a constant value of B orders the A and T_2 parameters, such that the A and T_2 values for the mixtures are intermediate between the respective A and T_2 parameters for the pure components. This means that the A and T_2 parameters for any of the liquids are given approximately by

$$A = \Sigma X_i A_i \tag{6}$$

$$T_2 = \Sigma X_i T_{2i} \tag{7}$$

where subscript i refers as before to pure component i. A_i and T_{2i} values were obtained by linear least squares fits to

Eqs. (6) and (7) of the A and T_2 values in Table V. These fits gave

$$A_{ND} = -7.869 \quad , \quad T_{2,ND} = 88.1$$

$$A_{NBC} = -7.705 \quad , \quad T_{2,NBC} = 101.1 \quad\quad (8)$$

$$A_{CD} = -7.170 \quad , \quad T_{2,CD} = 119.1$$

$$B = 641.1$$

Substituting Eqs. (6) and (7) into Eq. (2) gives immediately a semi-empirical equation which accounts for the combined composition/temperature dependence of viscosity:

$$\ln\eta(P) = \Sigma X_i A_i + B/(T(K) - \Sigma X_i T_{2i}) \quad\quad (9)$$

In Table VI are listed ratios of the viscosity calculated via Eq. (9) using the parameters of Eq. (8) to the experimental viscosity. Clearly Eq. (9) does not give a perfect account of the viscosity data. Pure component viscosities are underestimated, mixture viscosities generally overestimated, and the disagreement between experimental and calculated η's is largest at low temperatures where the differences in pure component η's are largest.

On the other hand, we feel that Eq. (9) gives a remarkably good account of the data. It describes the viscosities of both pure liquids and mixtures as a function of temperature using two fewer adjustable parameters than are required to account for η as a function of T of the pure liquids alone. This fit applies

to data covering a range of 4.54 in $\ell n\eta$. The mean deviation of $\ell n\eta$ from the fit is only 0.06 (i.e., about 6% in $\ln\eta$) and for the worst data point the deviation in $\ell n\eta$ is only 0.16.

Free Volume Interpretation of Viscosity

Equation (9) has previously been applied with success to viscosities of mixtures of perhydrodinorbornadienes (PHDNBD)[2-4] and to mixtures of PHDNBD's with exo-tetrahydrodicyclopentadiene (XTHDCPD),[2,3] hydrocarbons used as high energy density missile fuels. In Refs. 2 and 4 it was noted that Eq. (9) could be derived by combining the assumption of additivity of free volumes when the pure liquids are mixed with the assumption of logarithmic additivity of viscosities. In particular it was noted that the T_{2i} parameter could be interpreted as the temperature at which the free volume of liquid i vanishes at equilibrium. The other two parameters in Eq. (9) are given by[4,5]

$$A_i = \ell n\left[\frac{1}{\beta a_{0i}^2}\left(\frac{km_i}{8\pi}\right)^{1/2}\right] + \frac{1}{2}\left(1 + \ell nT - \frac{T_{2i}}{T}\right) \tag{10}$$

$$B = \frac{\gamma V^*}{V\Delta\alpha} - \frac{(T - T_{2i})^2}{2T} \tag{11}$$

where V = volume

V* = minimum local free volume for molecular diffusive step

$\Delta\alpha$ = difference between liquid and glass thermal expansion coefficients

γ = constant of the order of unity

a_{0i} = diameter of molecule i

β = fraction of a_{0i} travelled in a diffusive step

k = Boltzmann constant

m_i = mass of molecule i

The temperature dependences of A_i and B in Eqs. (10) and (11) are negligible in the temperature range of this study.

In Table VII we show molecular diameters a_{0i} calculated at 0°C for ND, NBC and CD from Eq. (10) and the A_i parameters of Eq. (8) using 0.2 for the value of β.[4,5] These are compared with mean molecular diameters calculated from the densities at 0°C, $(M/\rho_0 N_A)^{1/3}$, where M is molecular weight and N_A Avogadro's number. Also listed in Table VII are molecular dimensions L, W, H obtained from scale models[4] of the molecules. The CD molecule is rigid, but ND and NBC are flexible and possess a number of configurations. For ND the molecular dimensions are averages over four different configurations expressed in terms of the trans (t) or gauche (g) arrangement of groups bonded to adjacent carbons along the backbone of the molecule. These four ND configurations were all t, g at C's 5-6, g at C's 3-4 and 7-8, and g at C's 2-3, 5-6 and 8-9. For NBC the configuration was that shown on p. 1, with the n-butyl group occupying an equatorial position on the cyclohexane ring and the terminal $-CH_2CH_3$ group and cyclohexane ring in the trans position relative to each other. For this general NBC configuration molecular dimensions were the averaged for the t and g configurations of the groups bonded to C's 2-3 of the n-butyl side group. The molecular diameters from viscosity a_{0i} are

remarkably close to realistic molecular diameters. They correlate best with the maximum molecular dimensions L obtained from the models, as shown by the near constancy of the $a_{0\,i}/L$ ratio. These results are similar to those obtained for the rigid PHDNBD molecules,[2,4] for which nearly constant $a_{0\,i}/L$ values in the range 0.84 - 0.87 were obtained. As noted in Ref. 4, the constancy of the $a_{0\,i}/L$ values implies, via the free volume theory, that the critical sized void into which a molecule makes a diffusive step must be of sufficient size to accomodate the longest dimension of the molecule. This suggests in turn that the molecules are freely rotating in the viscosity range studied here.

For the PHDNBD isomers[2,4] the $T_{2\,i}$ values in Eq. (9) were all the same, so that the differences in viscosities of the isomers were accounted for strictly by differences in the A_i of Eq. (9) and hence by differences in the maximum molecular dimensions L. For the three C_{10} molecules considered here, differences in viscosities are due to differences both in the A_i and $T_{2\,i}$ parameters. Of these liquids ND and CD differ most in viscosity, by a factor of 3.0 at our upper temperature limit of 50°C and by a factor of 9.7 at the lower limit of about -55°C (extrapolating the ND viscosity via Eq. (2)). The differences in the A_i of ND and CD (and hence the differences in L) account for a factor of 2.0 difference in viscosity, i.e., for a substantial fraction of the viscosity difference in the experimental range. In view of the simplicity of the free volume model for viscosity of liquids, we feel that this is a

remarkable correlation between molecular structure and viscosity.

STUDIES PRESENTLY UNDERWAY

As noted above, Eq. (9) can be rationalized by combining the assumption of additivity of free volumes with the assumption of logarithmic additivity of viscosity. In view of the better success of Eq. (4) compared to Eq. (5) in correlating the isothermal composition dependence of viscosity, an alternative to Eq. (9) is suggested which combines the assumptions of additivity of free volumes and of fluidities. This would lead to a master viscosity equation of the form:

$$1/\eta = \left[\Sigma X_i \exp(-A_i) \right] \exp\left[-B/(T - \Sigma X_i T_{2\,i}) \right] \tag{12}$$

Rough preliminary calculations indicate that Eq. (12) does in fact work better than Eq. (9). At the present we are engaged in obtaining a computer fit of both Eqs. (9) and (12) to the viscosities of all the liquids listed in Table II.

REFERENCES

1. C. T. Moynihan, J. Phys. Chem., 70, 3399 (1966).

2. C. T. Moynihan, Proceedings of the NAVAIR-NRL Workshop on Basic Research Needs for Synthetic Hydrocarbon Jet Aircraft Fuels, Naval Research Laboratory, Washington, D. C., June 15-16, 1978, pp. 210-19.

3. C. T. Moynihan, U. E. Schnaus, H. Sasabe and D. Czaplak, Final Tech. Rept., NAVAIR Contract N00019-77-0065, December, 1977.

4. C. T. Moynihan, U. E. Schnaus and D. Czaplak, J. Phys. Chem., 82, 1087 (1978).

5. M. Cukierman, J. W. Lane and D. R. Uhlmann, J. Chem. Phys., 59, 3639 (1973).
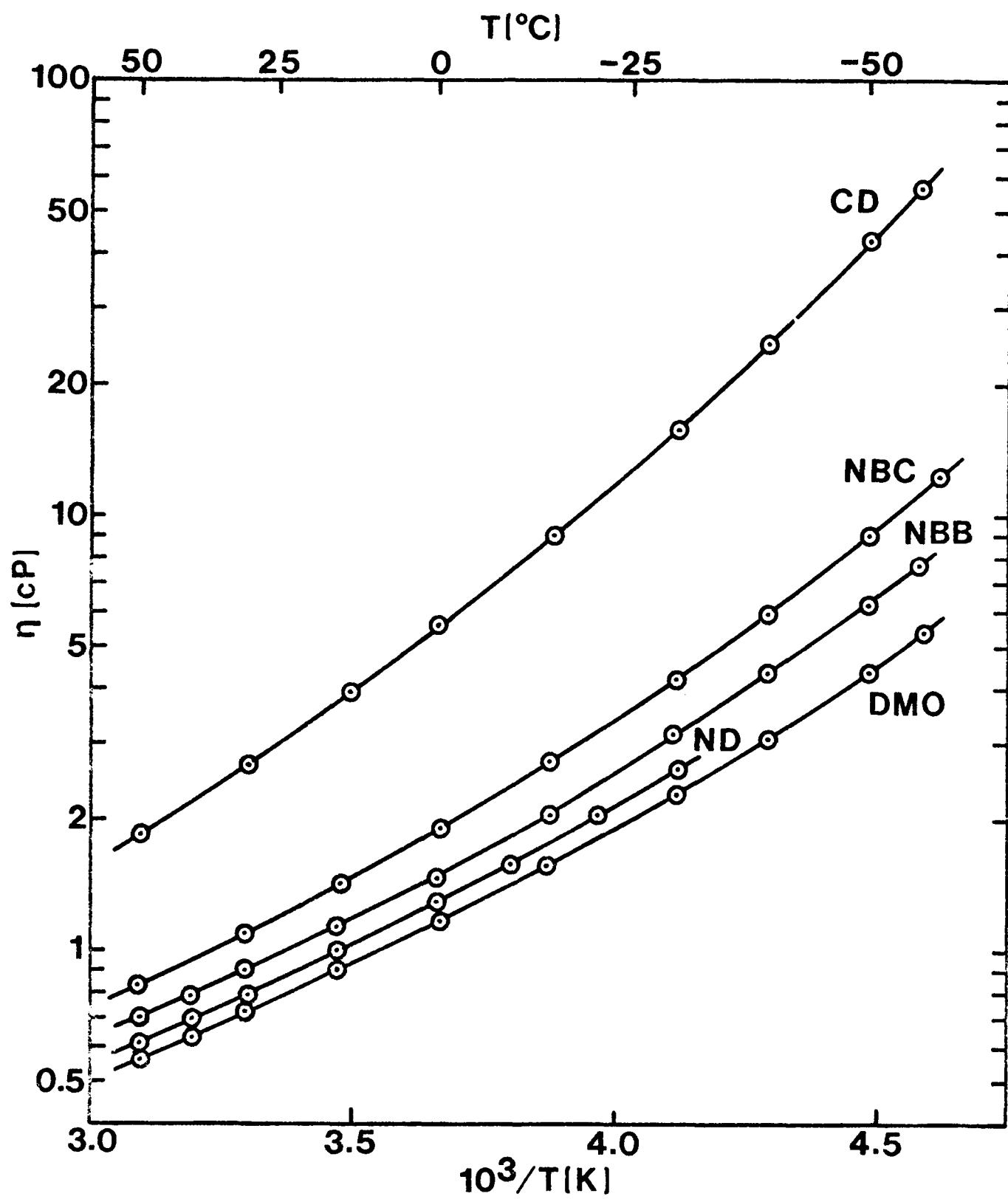
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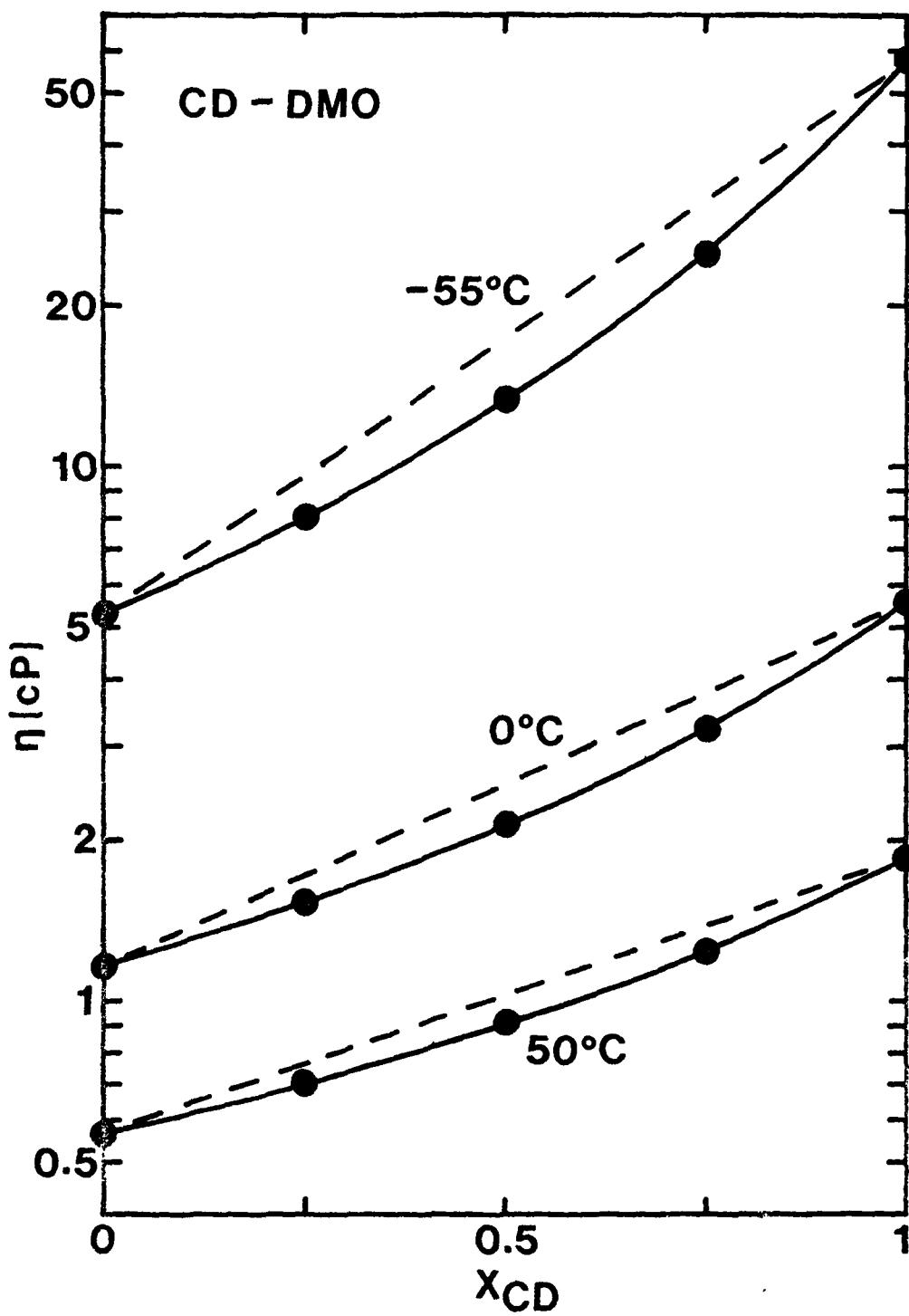
Fig. 2

TABLE I. Parameters for density equations for ND, NBC, CD, DMO, NBB, and their mixtures.

$$\rho\,(g/cm^3) \;=\; \rho_0 - bT(^\circ C)$$

Molar Composition	T range (°C)	ρ_0	$10^4\ b$	Standard Dev. ρ
ND (Run I)	−31 to 50	0.7447	7.44	0.0001
(Run II)	−31 to 50	0.7444	7.41	0.0002
NBC (Run I)	−57 to 50	0.8135	7.35	0.0001
(Run II)	−59 to 50	0.8139	7.37	0.0002
CD (Run I)	−55 to 50	0.9114	7.59	0.0002
(Run II)	−56 to 50	0.9096	7.54	0.0003
DMO	−56 to 50	0.7383	7.39	0.0002
NBB (Run I)	−55 to 50	0.8752	7.77	0.0001
(Run II)	−54 to 50	0.8753	7.87	0.0001
0.5 ND − 0.5 NBC				
(Run I)	−40 to 50	0.7780	7.36	0.0002
(Run II)	−40 to 50	0.7776	7.38	0.0001
0.5 ND − 0.5 CD	−40 to 50	0.8195	7.36	0.0002
0.5 ND − 0.5 DMO	−50 to 50	0.7417	7.35	0.0002
0.5 ND − 0.5 NBB	−45 to 50	0.8020	7.58	0.0002
0.5 NBC − 0.5 CD	−55 to 50	0.8598	7.39	0.0002

Table I (continued)

Molar Composition	T range (°C)	ρ_0	10^4 b	Std. Dev. ρ
0.5 NBC – 0.5 DMO	−56 to 50	0.7743	7.23	0.0003
0.5 NBC – 0.5 NBB	−53 to 50	0.8423	7.60	0.0003
0.75 CD – 0.25 DMO	−54 to 50	0.8613	7.41	0.0002
0.5 CD – 0.5 DMO	−55 to 50	0.8158	7.24	0.0002
0.25 CD – 0.75 DMO	−53 to 50	0.7755	7.33	0.0002
0.5 CD – 0.5 NBB	−54 to 50	0.8920	7.67	0.0002
0.5 DMO – 0.5 NBB	−55 to 50	0.7991	7.61	0.0001
1/3 ND – 1/3 NBC – 1/3 CD	−50 to 50	0.8176	7.35	0.0001
1/3 ND – 1/3 NBC – 1/3 NBB	−55 to 50	0.8059	7.49	0.0002
1/3 ND – 1/3 CD – 1/3 NBB	−51 to 50	0.8352	7.47	0.0002
1/3 NBC – 1/3 CD – 1/3 NBB	−55 to 50	0.8641	7.52	0.0002
0.25 ND – 0.25 NBC – 0.25 CD – 0.25 NBB	−55 to 50	0.8297	7.47	0.0002
0.2 ND – 0.2 NBC – 0.2 CD – 0.2 DMO – 0.2 NBB	−56 to 50	0.8094	7.41	0.0002

TABLE II. Best fit VTF equation parameters for shear viscosity of ND, NBC, CD, DMO, NBB, and their mixtures.

$$\ln \eta(P) = A + B/(T(K) - T_2)$$

Molar Composition	T range (°C)	A	B	T_2	Standard Dev. $\ln \eta$
ND (Run I)	-31 to 50	-7.7764	614.11	94	0.001
(Run II)	-31 to 50	-7.7442	605.03	95	0.002
NBC (Run I)	-57 to 50	-7.3986	549.44	113	0.004
(Run II)	-59 to 50	-7.3679	541.14	114	0.004
CD (Run I)	-55 to 50	-7.6572	796.29	106	0.004
(Run II)	-56 to 50	-7.6540	795.18	106	0.005
DMO	-56 to 50	-7.6158	534.10	104	0.005
NBB (Run I)	-55 to 50	-7.2973	483.68	116	0.003
(Run II)	-54 to 29	-7.1709	451.68	120	0.001
0.5 ND - 0.5 NBC					
(Run I)	-40 to 50	-7.6013	584.93	102	0.002
(Run II)	-40 to 50	-7.6843	613.23	98	0.003
0.5 ND - 0.5 CD	-44 to 50	-7.6322	663.30	98	0.004
0.5 ND - 0.5 DMO	-50 to 50	-7.6243	547.89	103	0.004
0.5 ND - 0.5 NBB	-45 to 50	-7.5610	554.51	100	0.003
0.5 NBC - 0.5 CD	-55 to 50	-7.5108	658.00	108	0.003
0.5 NBC - 0.5 DMO	-56 to 50	-7.4730	529.26	110	0.005
0.5 NBC - 0.5 NBB	-53 to 50	-7.4491	549.18	106	0.004
0.75 CD - 0.25 DMO	-54 to 50	-7.5650	686.71	107	0.002
0.5 CD - 0.5 DMO	-55 to 50	-7.5067	604.51	108	0.003
0.25 CD - 0.75 DMO	-53 to 50	-7.5645	565.81	106	0.004
0.5 CD - 0.5 NBB	-54 to 50	-7.2042	543.55	114	0.003
0.5 DMO - 0.5 NBB	-55 to 50	-7.4655	511.02	106	0.004
1/3 ND - 1/3 NBC - 1/3 CD	-50 to 50	-7.5518	621.52	104	0.003
1/3 ND - 1/3 NBC - 1/3 NBB	-55 to 50	-7.5352	562.32	102	0.003
1/3 ND - 1/3 CD - 1/3 NBB	-51 to 50	-7.4812	586.03	103	0.002
1/3 NBC - 1/3 CD - 1/3 NBB	-55 to 50	-7.4028	584.63	108	0.004
0.25 ND - 0.25 NBC - 0.25 CD - 0.25 NBB	-55 to 50	-7.4598	577.65	105	0.003
0.2 ND - 0.2 NBC - 0.2 CD - 0.2 DMO - 0.2 NBB	-56 to 50	-7.4569	554.62	107	0.004

TABLE III. Comparison of results of duplicate viscosity experiments.

Molar Composition	T(°C)	n (cP) Run I	Run II	% diff.
ND	50	0.612	0.614	0.3
	0	1.291	1.292	0.1
	-30	2.572	2.569	0.1
NBC	50	0.836	0.839	0.4
	0	1.889	1.890	0.1
	-30	4.16	4.16	0.0
	-55	11.35	11.37	0.2
CD	50	1.848	1.844	0.2
	0	5.53	5.51	0.4
	-30	15.67	15.59	0.5
	-55	57.1	56.7	0.7
NBB	30	0.897	0.905	0.9
	0	1.469	1.467	0.1
	-30	3.036	3.010	0.9
	-55	7.69	7.66	0.4
0.5 ND - 0.5 NBC	50	0.703	0.700	0.4
	0	1.523	1.524	0.1
	-30	3.147	3.140	0.2
	-40	4.32	4.29	0.7

TABLE IV. Tests of isothermal additivity rules for shear viscosities of mixtures of C_{10} hydrocarbons. n_{ex} is the experimental mixture viscosity.

Molar Composition	$(\Sigma X_i/n_i)^{-1}/n_{ex}$		$\exp(\Sigma X_i \ln n_i)/n_{ex}$	
	50°C	−30°C	50°C	−30°C
0.5 ND − 0.5 NBC	1.00	1.01	1.02	1.04
0.5 ND − 0.5 CD	1.00	0.95	1.15	1.36
0.5 ND − 0.5 DMO	1.00	0.99	1.00	1.00
0.5 ND − 0.5 NBB	1.05	1.11	1.05	1.12
0.5 NBC − 0.5 CD	0.99	0.93	1.07	1.14
0.5 NBC − 0.5 DMO	0.99	0.98	1.01	1.02
0.5 NBC − 0.5 NBB	1.04	1.10	1.05	1.12
0.5 CD − 0.5 DMO	0.95	0.83	1.12	1.25
0.5 CD − 0.5 NBB	1.02	1.02	1.14	1.38
0.5 DMO − 0.5 NBB	1.04	1.10	1.04	1.11
1/3 ND − 1/3 NBC − 1/3 CD	0.99	0.95	1.10	1.21
1/3 ND − 1/3 NBC − 1/3 NBB	1.04	1.09	1.05	1.11
1/3 ND − 1/3 CD − 1/3 NBB	1.04	1.04	1.15	1.34
1/3 NBC − 1/3 CD − 1/3 NBB	1.03	1.04	1.12	1.26
0.25 ND − 0.25 NBC − 0.25 CD − 0.25 NBB	1.03	1.04	1.11	1.26
0.2 ND − 0.2 NBC − 0.2 CD − 0.2 DMO − 0.2 NBB	1.02	1.01	1.10	1.21

TABLE V.   VTF equation parameters for shear viscosity of
ND, NBC, CD, and their mixtures for constant B parameter.

$$\ln \eta(P) = A + B / (T(K) - T_2)$$

Molar Composition	T range (°C)	A	B	T_2	Std. Dev. $\ln \eta$
ND	-31 to 50	-7.848	641.1	90.1	0.002
NBC	-57 to 50	-7.699	641.1	101.8	0.013
CD	-55 to 50	-7.127	641.1	121.1	0.022
0.5 ND - 0.5 NBC	-40 to 50	-7.761	641.1	94.2	0.004
0.5 ND - 0.5 CD	-44 to 50	-7.567	641.1	100.8	0.004
0.5 NBC - 0.5 CD	-55 to 50	-7.455	641.1	109.9	0.004
1/3 ND - 1/3 NBC - 1/3 CD	-50 to 50	-7.612	641.1	101.6	0.004

TABLE VI. Ratios of viscosities calculated from master viscosity equation (Eq. (9)) to experimental viscosities for ND, NBC, CD, and their mixtures.

$$\eta_{calc} / \eta_{ex}$$

Molar Composition	@ 50°C	@ -30°C	@ -50°C
ND	0.96	0.93	----
NBC	0.97	0.99	0.96
CD	0.96	0.86	0.86
0.5 ND - 0.5 NBC	0.98	0.99	----
0.5 ND - 0.5 CD	1.09	1.15	----
0.5 NBC - 0.5 CD	1.03	1.03	1.04
1/3 ND - 1/3 NBC - 1/3 CD	1.04	1.08	1.09

TABLE ?II. Comparison of molecular diameters of $C_{?}$ hydrocarbons estimated from viscosity with those estimated from diffusion and molecular models.

Molecule	a_{oi} (nm)	$(3V/4\pi N_A)^{1/3}$ (nm)	L, W, H (nm) from models	a_{oi}
ND	1.04	0.68	1.35, 0.57, 0.52	0.7?
HBC	0.95	0.66	1.18, 0.69, 0.53	0.8
?D	0.71	0.63	0.97, 0.75, 0.52	0.7